Characterization of Carbon Films on the Japanese Smoked Roof Tile "Ibushi-Kawara" by High-Resolution Soft X-ray Spectroscopy

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Carbon films on the Japanese smoked roof tile "Ibushi-Kawara" were characterized by high-resolution soft X-ray spectroscopy using synchrotron radiation. By comparing the soft X-ray emission and absorption spectra of Kawara with the reference carbon compounds, it was determined that the carbon films on Kawara consist of mostly carbon-black-like sp^2 carbon atoms and that the surface also contains polyethylene-like sp^3 carbon atoms. The take-off/incident-angle dependence on the X-ray emission/absorption spectra of Kawara shows that the carbon-black-like sp^2 carbon atoms partially form a layer structure oriented parallel to the basal clay plane, and that the degree of orientation of the carbon films is estimated to be 50% that of highly oriented pyrolytic graphite (HOPG). The microstructure of the carbon films on Kawara is one in which half of the carbon-black-like sp^2 carbon atoms form layer-structured clusters parallel to the basal clay plane and the rest of the carbon atoms form random-structured clusters which rigidly connect the layer-structured clusters. [DOI: 10.1143/JJAP.42.6551]

KEYWORDS: carbon, roof tile, soft X-ray, synchrotron radiation, X-ray emission, X-ray absorption

1. Introduction

The Japanese roof tile "Kawara" is generally made from sintered clay with coating materials on the surface. Typically, the Kawara tiles are manufactured in two steps. The first step is to shape the Kawara body from clay and then sinter it in a furnace at a temperature higher than 1000°C. Afterwards, the surface of the basal body is treated. One method for treating the surface is carbon coating by smoking with hydrocarbon gas, which can be regarded as the chemical vapor deposition (CVD) of hydrocarbons. The smoked Kawara is called "Ibushi-Kawara" which is a metallic oxidized-silver-colored tile and is very durable.

In 1978, carbon films on an Ibushi-Kawara were characterized by Motoyama[1] using electron probe microanalysis (EPMA), small-angle X-ray scattering, and transmission electron microscopy (TEM). This study revealed that the carbon films consisted of plane, spherical, and fibrous carbons. The plane carbon had a graphite-like layer structure, while both the spherical and fibrous carbons had carbon-black-like structures. Since then, few X-ray spectroscopic studies have focused on the carbon films of Ibushi-Kawara. To confirm the chemical bonding states and microstructure of the carbon films using advanced X-ray analysis methods, we characterized the carbon films by high-resolution soft X-ray spectroscopy using synchrotron radiation.[2,3] The chemical bonding states of the carbon films were determined by comparing the soft X-ray emission and absorption spectra between the carbon films and reference carbon compounds. Angle-resolved soft X-ray emission and absorption spectra also provide information on the microstructure. In this paper, we describe the soft X-ray emission and absorption spectra in the carbon (C) K region of the carbon films of Ibushi-Kawara (hereafter "Kawara") and determine their chemical bonding states and microstructures.

2. Experiments

Sample pieces of Kawara were quarried from the surface portion of commercially available Kawara for spectroscopic measurements. Figure 1 shows a scanning electron micro-
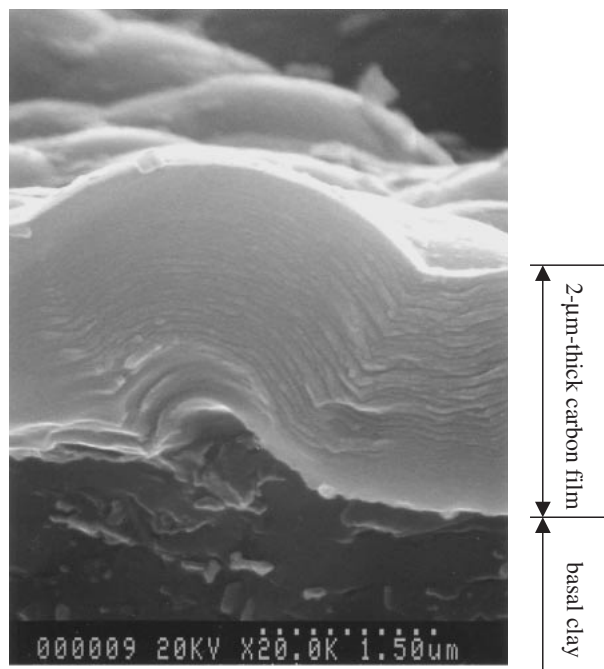

Fig. 1. Cross-sectional SEM image of the Kawara surface.

scopy (SEM) cross-sectional image of a Kawara sample, which illustrates that the surface carbon film was approximately 2 μm thick and the carbon film formed a macroscopic layer structure, which oriented nearly parallel to the basal clay plane. Highly oriented pyrolytic graphite (HOPG) and powder samples of diamond, carbon black, and polyethylene were also prepared as reference compounds.

Spectroscopic measurements of the soft X-ray emission and absorption in the CK region were performed at the advanced light source (ALS) of Lawrence Berkeley National Laboratory (LBNL). X-ray emission spectra were measured using a grating X-ray spectrometer installed in the undulator beamline, BL-8.0.1.[4] The photon energy of the monochromatized incident beam was tuned to 320 eV to effectively excite the C1s electrons and to prevent multiple ionizations.

The resolving power ($E/\Delta E$) of the spectrometer was estimated to be approximately 500 using a 50 μm entrance slit and a 600 line/mm spherical grating with a 10 m radius. Energy calibration was achieved by tuning the main peak energy of HOPG to 276.9 eV, referring to previously published spectra.[5] The total electron yield (TEY) X-ray absorption spectra were measured in a bending-magnet beamline, BL-6.3.2,[6] by monitoring the sample photocurrent. To effectively detect the photocurrent of the carbon films on Kawara, conductive tape was attached to the carbon films because the basal clay bodies were insulators. The powder samples of the reference compounds were pressed and held on indium plate substrates. The resolving power of the monochromatized incident beam was estimated to be 2000 using a 600 line/mm grating and a 20 μm slit. Energy calibration was achieved by tuning the π^* peak energy of HOPG to 285.5 eV, referring to previously published spectra.[7] In both BL-8.0.1 and BL-6.3.2, the electric field (E) vectors of the incident synchrotron radiation beams were in the horizontal plane. Therefore, the samples were rotated around the vertical axis to measure their angle-resolved X-ray emission and absorption spectra. For the X-ray emission measurements the take-off angles were 15°, 45°, and 75°. In the X-ray absorption measurements the incident angles were varied among 15°, 45°, 75°, and 90°. The geometries of the take-off/incident angles in the X-ray emission and absorption measurements are illustrated in the insets of Figs. 4 and 7, respectively.

3. Results and Discussion

3.1 Soft X-ray emission and absorption spectra

Figure 2 shows the CK X-ray emission spectra of the Kawara and reference compounds measured with a take-off angle of 45°. The Kawara spectrum exhibits a main peak at 277 eV and a high-energy shoulder near 281.5 eV, which correspond to the σ and π peaks in HOPG, respectively. However, the Kawara peak structure is broader than that of HOPG. The spectrum of carbon black also exhibits a main peak at 277 eV and a high-energy shoulder near 281.5 eV, which is broader than that of HOPG and agrees with the spectral feature of the Kawara. The spectrum of polyethylene, in which the main peak is observed at 279 eV, is significantly different from those of HOPG and carbon black. Thus we can rationalize that the carbon atoms of HOPG and carbon black have sp^2 structures and polyethylene has an sp^3 structure. By comparing the X-ray emission spectra of Kawara with these reference compounds, it is determined that the carbon films on Kawara are composed essentially of carbon-black-like sp^2 carbon atoms and the presence of polyethylene-like sp^3 carbon atoms is negligible in the X-ray emission spectrum of Kawara.

Figure 3 shows the TEY X-ray absorption spectra of the Kawara and reference compounds measured with an incident angle of 45°. The Kawara spectrum has two sharp peaks at 285.5 eV and 287.8 eV and a broader peak at 293 eV. By comparing with the HOPG spectrum, the 285.5 eV and 293 eV peaks in Kawara are assigned to the π^* peak and the σ^* peak, respectively. These π^*- and σ^*-peak structures show that the majority of the carbon atoms in Kawara have sp^2 structures. Both the π^* and σ^* peaks in Kawara are, however, broader than those of HOPG. The spectrum of carbon black
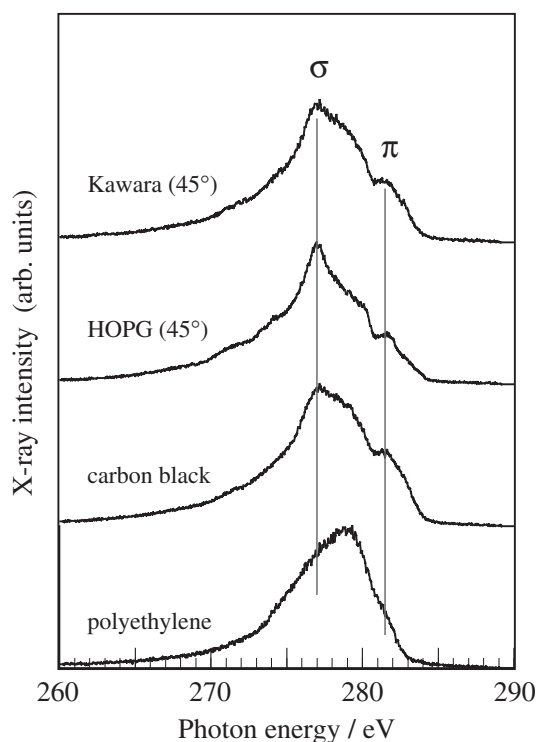

Fig. 2.   CK X-ray emission spectra of the carbon films on Kawara and the reference compounds. The excitation energy is tuned to 320 eV. The take-off angles of emitted X-rays are fixed at 45°.
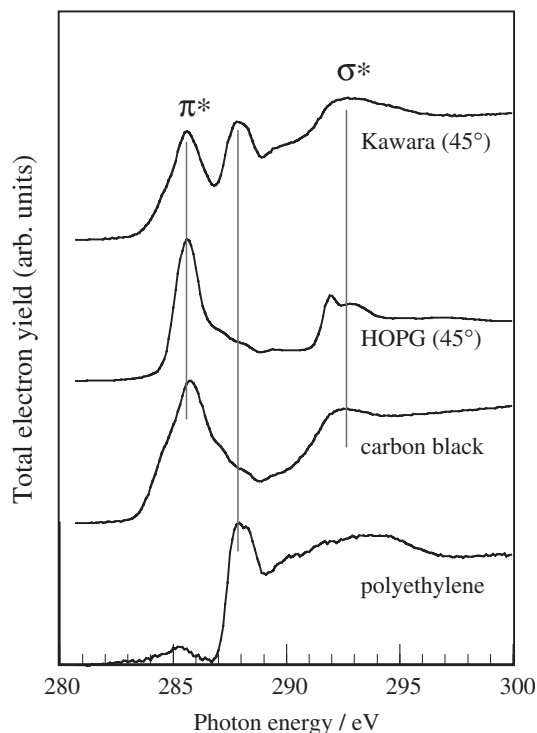

Fig. 3.   Total electron yield (TEY) X-ray absorption spectra in the CK region of the carbon films on Kawara and the reference compounds. The incident angle of the monochromatized synchrotron radiation beam is fixed at 45°.

exhibits a π^* peak at 285.5 eV and a σ^* peak at 293 eV. These peaks are broader than that of HOPG and their peak energies correspond to the energies of the Kawara peaks except for the 287.8 eV peak. The 287.8 eV peak in Kawara corresponds to

the threshold peak in polyethylene, and the Kawara spectral features are reproduced by combining the carbon black and polyethylene spectra. The TEY X-ray absorption spectrum of Kawara shows that the carbon films on Kawara are composed of carbon-black-like sp^2 carbon atoms and polyethylene-like sp^3 carbon atoms.

It is well known that soft X-ray emission measurements are bulk sensitive and TEY absorption measurements are surface sensitive. In the CK region the detection depth of the X-ray emission in carbon materials can be estimated to be several hundred Å, while that of the TEY X-ray absorption can be estimated to be only several Å. The data from the measured X-ray emission and absorption spectra reveal that the carbon films on the Kawara are composed of carbon-black-like sp^2 carbon atoms and that some polyethylene-like sp^3 carbon atoms which may be formed and deposited in the low-temperature annealing during the smoking process are on the surface.

3.2 Angle-resolved soft X-ray emission and absorption spectra

Monsour[8] previously presented the theoretical expression for the contribution of σ and π orbitals to the X-ray emission spectra of graphite. Generally, fluorescent X-rays emit perpendicular to the orbital direction, which results from electric dipole transitions in the participating orbitals. In graphite, the σ orbitals are perpendicular to the c-axis and the π orbitals are parallel to the c-axis. Considering this orbital geometry, the CK X-ray emission intensity of graphite, I_{emi} (E, θ_t), which depends on the photon energy (E) and take-off angle (θ_t), is given by a linear combination of the σ and π emission intensities as described by

$$I_{\text{emi}}(E, \theta_\text{t}) = I_{\sigma\text{emi}}(E)\{(1 + \cos^2 \theta_\text{t})/2\} + I_{\pi\text{emi}}(E)\sin^2 \theta_\text{t}, \quad (1)$$

where $I_{\sigma\text{emi}}$ (E) and $I_{\pi\text{emi}}$ (E) are the X-ray intensities originating from the σ and π orbitals, respectively. The CK X-ray emission intensity is generally proportional to the C2p density of states (DOS). Therefore, the take-off-angle dependence of the calculated X-ray emission spectra is obtained from eq. (1) by replacing $I_{\sigma\text{emi}}$ (E) and $I_{\pi\text{emi}}$ (E) with the σ and π portions of the occupied C2p-DOS, respectively. The peak intensity ratio of the π relative to the σ portions, $(\pi/\sigma)_{\text{emi}}$, is expressed by

$$(\pi/\sigma)_{\text{emi}} = \{I_{\pi\text{emi}}(E)\sin^2 \theta_\text{t}\}/[I_{\sigma\text{emi}}(E)\{(1 + \cos^2 \theta_\text{t})/2\}]$$
$$= K \sin^2 \theta_\text{t}/(1 + \cos^2 \theta_\text{t}), \quad (2)$$

where K is described as $2I_{\pi\text{emi}}(E)/I_{\sigma\text{emi}}(E)$. In X-ray absorption, the polarized incident X-rays are absorbed by the orbitals projected in the E-vector direction of the incident X-rays. Using the analogy of the above-mentioned X-ray emission, the X-ray absorption intensity, I_{abs} (E, θ_i), which depends on the photon energy (E) and incident angle (θ_i), is expressed as

$$I_{\text{abs}}(E, \theta_\text{i}) = I_{\sigma\text{abs}}(E)\{(1 + \sin^2 \theta_\text{i})/2\} + I_{\pi\text{abs}}(E)\cos^2 \theta_\text{i}, \quad (3)$$

where $I_{\sigma\text{abs}}$ (E) and $I_{\pi\text{abs}}$ (E) are the X-ray absorption intensities from σ and π orbitals, respectively. The peak intensity ratio, $(\pi/\sigma)_{\text{abs}}$, in the absorption spectra is expressed by
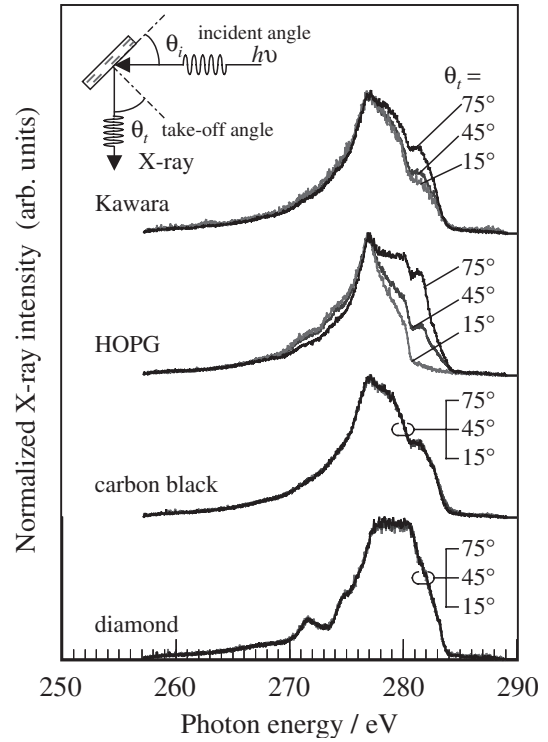

Fig. 4. Take-off-angle-resolved CK X-ray emission spectra of Kawara and the reference compounds. The take-off angles are varied to 15°, 45°, and 75°.

$$(\pi/\sigma)_{\text{abs}} = \{I_{\pi\text{abs}}(E)\cos^2 \theta_\text{i}\}/[I_{\sigma\text{abs}}(E)\{(1 + \sin^2 \theta_\text{i})/2\}]$$
$$= K \cos^2 \theta_\text{i}/(1 + \sin^2 \theta_\text{i}), \quad (4)$$

where K is described as $2I_{\pi\text{abs}}(E)/I_{\sigma\text{abs}}(E)$.

Figure 4 shows the take-off-angle-dependent CK X-ray emission spectra of Kawara and reference compounds. The peak intensities of the high-energy shoulders, which are assigned to the π peaks, in Kawara and HOPG increase as the take-off angle increases. This take-off-angle dependence in the X-ray emission spectra of HOPG agrees with the previously measured angle-dependent spectra[5] and is explained by the anistropy of the σ and π orbitals of the sp^2 carbon atoms in the layer structure. The take-off-angle dependence of Kawara implies that the carbon atoms partially take a layer structure oriented parallel to the basal clay plane. In the spectra of carbon black and diamond, take-off-angle dependence is not observed because carbon black has an amorphous structure and diamond consists of isotropic sp^3 carbons. In order to compare the orientation of the carbon films on Kawara with HOPG, the σ and π portions in their spectra are experimentally separated as shown in Fig. 5. The upper panels show the CK X-ray emission spectra of HOPG and Kawara measured with take-off angles of 15° and 75°, and their subtracted spectra, (75°)–(15°), which show the π portion. In HOPG, the subtracted spectrum exhibits a triangular shape with a 282 eV peak and low-energy tailing, which agrees with the π portion of the calculated C2p-DOS.[9] The subtracted Kawara spectrum exhibits a similar triangular shape with a 282 eV peak and low-energy tailing, but is broader than HOPG. Based on the spectral feature of the π portions, the σ portions can also be separated from the CK X-ray emission spectra. The lower panels of Fig. 5 show the
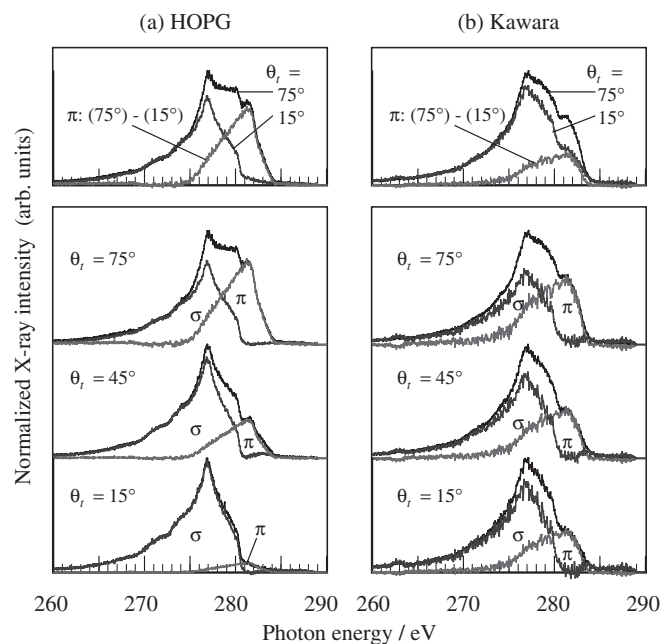
Fig. 5. Separation of π and σ portions from the CK X-ray emission spectra of HOPG and Kawara. The upper panels show the π portions obtained from the subtracted spectra of $(75°)$–$(15°)$. The lower panels show the separation of π and σ portions in the X-ray emission spectra measured with take-off angles of $15°$, $45°$, and $75°$.
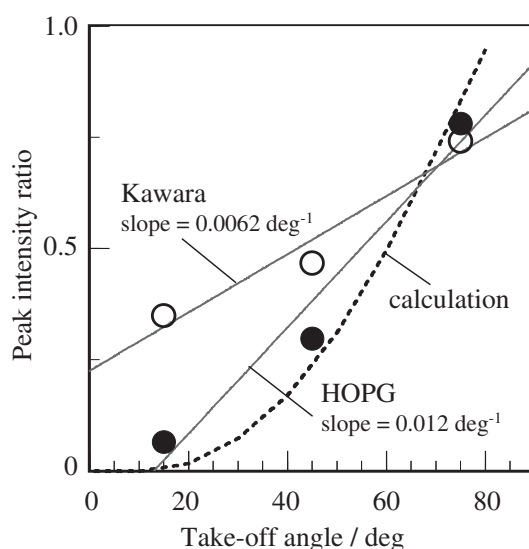

Fig. 6. Take-off-angle dependence of the peak intensity ratio of π and σ portions in the CK X-ray emission spectra of HOPG and Kawara. The broken line shows the take-off-angle-dependence of the calculated peak intensity ratio, $(\pi/\sigma)_{\mathrm{emi}}$, in graphite.

individual contributions of the σ and π portions in the CK X-ray emission spectra of HOPG and Kawara measured at $15°$, $45°$, and $75°$. The σ portions in HOPG exhibit a sharp peak at 277 eV with a high-energy shoulder and low-energy tailing. This spectral feature is reproduced by the σ portion of the calculated C2p-DOS which has an intense peak with a high-energy peak and low-energy peaks. The σ portion of Kawara also exhibits a similar shape which has the 277-eV peak with a high-energy shoulder and low-energy tailing, but is broader than HOPG. The peak intensity ratio of the π and σ portions in the X-ray emission spectra, $(\pi/\sigma)_{\mathrm{emi}}$, are obtained from the experimentally separated σ- and π-portion areas. Figure 6 shows the measured take-off-angle dependence of the peak intensity ratio in HOPG and Kawara. The calculated take-off-angle dependence of ideally oriented graphite, which is obtained from eq. (2), is described by a broken line and agrees with the measured HOPG data. In order to compare the orientation of the carbon films for Kawara and HOPG, the take-off-angle dependences of the peak intensity ratios in Kawara and HOPG are approximated with linear functions. If a carbon material does not have an oriented layer structure, then the slope of the approximated linear functions is zero. Therefore, the slope provides the degree of orientation for the carbon layers. The slope of HOPG ($0.012\,\mathrm{deg}^{-1}$) is twice that of Kawara ($0.0062\,\mathrm{deg}^{-1}$), which indicates that the orientation of the carbon films on Kawara is 50% of the HOPG.

Figure 7 shows the incident-angle-resolved TEY X-ray absorption spectra of Kawara and the reference compounds. In the spectra, the intensities are normalized at the σ^* peaks near 293 eV. In Kawara, the relative peak intensity of the π^* peak at 285.5 eV clearly increases as the incident angle decreases from $90°$ to $15°$, but that the 287.8 eV peak, which is due to polyethylene-like sp^3 carbon, is independent of the angle. In the spectra of HOPG, the relative peak intensity of
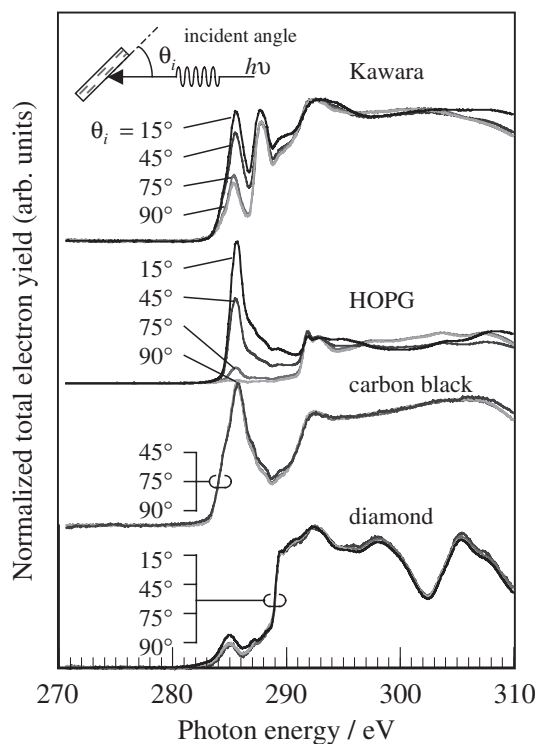

Fig. 7. Incident-angle-resolved TEY X-ray absorption spectra of Kawara and the reference compounds. The incident angles are varied to $15°$, $45°$, $75°$, and $90°$.

the π^* peak at 285.5 eV significantly increases as the incident angle decreases, which agree with the previously measured angle-dependent spectra.[7] It is well known that the incident-angle dependence on the X-ray absorption spectra of graphite results from the anistropy of the σ and π orbitals of the sp^2-carbon atoms in layer structures. In the spectra of carbon black and diamond, incident-angle dependence is not observed because carbon black has an amorphous structure
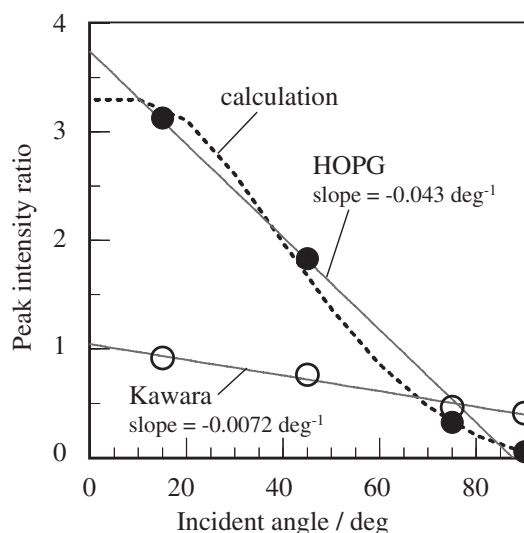
Fig. 8. Incident-angle dependence on the peak intensity ratio in the TEY X-ray absorption spectra of HOPG and Kawara. The broken line shows the incident-angle dependence of the calculated peak intensity ratio, $(\pi/\sigma)_{\mathrm{abs}}$, in graphite.

and diamond consists of isotropic sp^3 carbons. The incident-angle dependence of the peak intensity ratio, $(\pi/\sigma)_{\mathrm{abs}}$, in Kawara is similar to that of HOPG, which suggests that the carbon films on Kawara patially have a layer structure oriented parallel to the basal clay plane. Figure 8 shows the incident-angle dependence of the peak intensity ratio of HOPG and Kawara measured from Fig. 7. The calculated peak intensity ratio of ideally oriented graphite, which is obtained from eq. (4), is described by a broken line and agrees with the measured HOPG data. In order to estimate the orientation of the carbon films on Kawara, the measured incident-angle dependence of the peak intensity ratio in Kawara and HOPG are approximated as linear functions. The slope of the HOPG linear function is $-0.043\,\mathrm{deg}^{-1}$ and that of Kawara is $-0.0072\,\mathrm{deg}^{-1}$, which shows that the orientation of the carbon films on Kawara is 17% of HOPG. The orientation of the carbon films obtained from the TEY X-ray absorption measurements was smaller than that from the X-ray emission measurements, which has been rationalized by the fact that the σ^* peak in the TEY X-ray absorption of Kawara results from both the carbon-black-like sp^2 carbon atoms and the polyethylene-like sp^3 carbon atoms. Consequently, the orientation of the carbon films is estimated to be 50% of HOPG from the X-ray emission measurements.

It is well known that carbon black consists essentially of polycyclic aromatic hydrocarbon (PHA) clusters with an average size of several nm[10] and it is reasonable to assume that the large PHA clusters in the carbon films form a preferred orientation similar to graphite. Therefore, the induced microstrucure of the carbon films on Kawara is one in which half of the carbon-black-like sp^2 carbon atoms form layer-structured clusters oriented parallel to the basal clay plane and the rest of the carbon atoms form random-structured clusters, which rigidly connect the layer-structured clusters. It is rationalized that the metallic oxidized-silver color of Kawara originates from the layer-structured clusters

in which π electrons behave just like free electrons in metals. The durability originates from the random-structured clusters.

4. Conclusions

High-resolution soft X-ray emission and absorption spectra in the CK region of the carbon films on the Japanese smoked roof tile, Ibushi-Kawara, and reference carbon compounds were measured using synchrotron radiation. The X-ray emission and absorption spectra elucidate that the carbon films on Kawara consist of carbon-black-like sp^2 carbon atoms and the surface also contains polyethylene-like sp^3 carbon atoms which may be formed in the low-temperature annealing process. The take-off/incident-angle dependence observed in the X-ray emission and absorption spectra of Kawara shows that the sp^2 carbon atoms partially take a layer structure oriented parallel to the basal clay plane. This finding of the oriented layer structure essentially agrees with a previous study.[1] From the take-off-angle dependence of the π/σ peak intensity ratio in the CK X-ray emission spectra of Kawara and HOPG, the orientation of the carbon films on Kawara is estimated to be 50% of HOPG. It has been concluded that half of the carbon atoms in Kawara form layer-structured clusters which give the metallic oxidized-silver color and the rest of the carbon atoms form random-structured clusters which make it durable.

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